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THE PRESSURE COEFFICIENT OF RESISTANCE OF FIFTEEN METALS DOWN TO LIQUID OXYGEN TEMPERATURES.

By P. W. BRIDGMAN.

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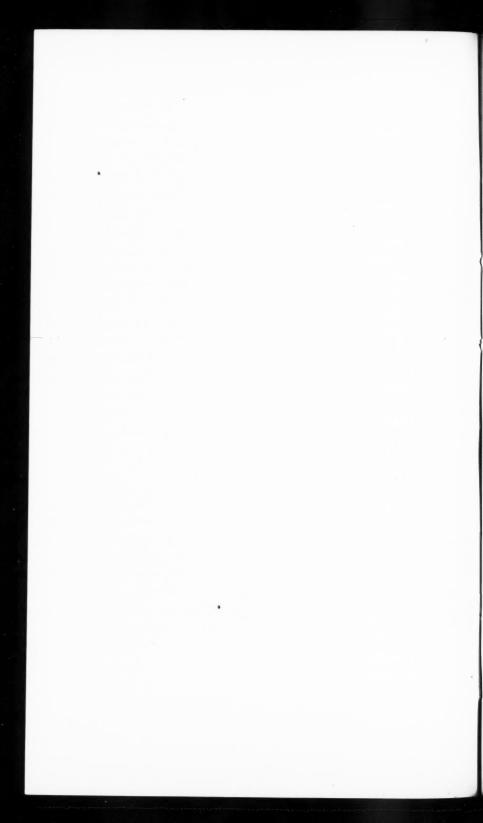


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#### TABLE OF CONTENTS.

	Pag	e
tion	30	5
ie	30	6
eral Technique		6
avior of Steel under High Helium Pressure		5
erimental Procedure	32	1
Presentation of Data	32	2
1		3
mesium .		4
ninum		5
or		6
		7
per.		7
el.		8
ndium.		
mbium.		_
num.		
dium	. , . ,	_
ybdenum.		_
		_
alum		
zsten	33	

#### Introduction.

It would be of great interest to determine the effects of high pressures on the properties of materials without any of the complications arising from thermal agitation, that is, at 0° Abs. Such measurements at absolute zero itself, or even within a few degrees of it, will probably, however, remain always impossible, not only because of the inaccessibility of the absolute zero, but because of other technical difficulties which will appear later, so that we will doubtless have to content ourselves with more moderate excursions into this field.

The measurements recorded in this paper are the first results of my attempt to combine high pressures and low temperatures. Technical difficulties were fully expected, but they proved to be even greater than anticipated, and the experiments have now been continued over several years. The net result is that I have now measured electrical resistance up to 7000 kg/cm² at liquid oxygen temperature, 90° Abs, and in this paper I present measurements on 15 metals over this range. The temperature limit has been set by the fact that only ordinary liquid air has been at my disposal; it is probable that the identical technique would permit measurements to several thousand kg/cm² at liquid hydrogen temperatures, were this available. The same apparatus should also serve with little modification for other sorts of measurement, such as thermal e.m.f.

In the following more attention than usual will be devoted to the technique used in entering this region.

#### TECHNIQUE.

General Technique. The most important difference between high pressure experiments at ordinary temperatures and at low temperatures is at once obvious in the restriction on the fluids which can be used for transmitting hydrostatic pressure. At room temperature, ordinary liquids, such as the lighter hydrocarbons, may be employed up to pressures of 12000 or 15000 kg/cm<sup>2</sup>. The range is limited either by freezing or by too great an increase of viscosity, which is greatly affected by pressure. At liquid air temperatures, freezing occurs at much lower pressures, and an inspection of tables of melting points. as in International Critical Tables, will show at once that there is no known substance liquid under ordinary conditions which will remain liquid at liquid air temperatures over any pressure range worth considering. It is necessary, therefore, to have recourse to the so-called permanent gases, and even here the possibilities are very limited. Work by Simon and collaborators1 on the solidification of gases under pressure shows that nitrogen, for example, solidifies at a pressure of 1500 kg/cm<sup>2</sup> at 90° Abs, and that the only possibilities are helium and hydrogen. Of these hydrogen can be at once eliminated because of its chemical attack on steel at high pressures, 2 it being impossible to retain without rupture a pressure of more than 9000 kg of hydrogen in a steel vessel, even for a short time, and after prolonged use, the pressure of rupture may be very much lowered, with accompanying danger. Helium, then, remains the only possibility. Simon's

melting curves show by extrapolation that the freezing pressure of this at 90° Abs. is probably of the order of 15000 kg, thus making accessible a sufficiently wide pressure range. Fortunately helium is now sufficiently inexpensive so that it can be freely used in the laboratory, and an experiment which would have been absolutely out of the question several years ago, now at least enters the realm of possibility. The question had still to be answered, however, whether helium would penetrate steel like hydrogen; its chemical inertness offered

ground for optimism.

The use of a gas as pressure medium demands the use of precompressors in order to get sufficient volumes. The design of these is sufficiently straightforward, and will not be described in detail. Two such precompressors were used. The first receives the helium at tank pressure, initially 1600 1b/in<sup>2</sup>, which becomes less as the tank becomes exhausted. This first precompressor contains a single double-headed piston, with packing on both ends. Such an arrangement is better than the more usual mercury separator scheme, because there is no danger of mercury getting into wrong parts of the apparatus. One side of the piston is acted on by a suitable glycerine and water mixture from a hand pump, and the other end of the piston compresses the helium. The diameter of the piston is 11/4 inches, and the length of stroke 18 inches. The final pressure reached with this compressor is about 10000 lb/in2. The pump is one of the hand pumps which I have used in all my other high pressure work for actuating the various hydraulic intensifiers. Since use of a gas demands the handling of large volumes, this pump has been fitted with a motor drive, which may be detached at pleasure, with much success. Beyond the first precompressor is the second, which is one of the 4 to 1 intensifiers used in my other work and described elsewhere.3 There is a needle valve by which the first compressor is cut off during the action of the intensifier, and there are also valves by which the same pump which at first operated the separator may now operate the intensifier. The intensifier connects directly to the high pressure apparatus, through a bye-pass at the upper end of the working cylinder, exactly as in my other high pressure apparatus. The intensifier is operated to a pressure of about 2000 kg/cm<sup>2</sup>, and then the piston of the high pressure apparatus comes down, shutting off the bye-pass. The remainder of the high pressure range is reached with a single stroke of the high pressure piston. The working high pressure cylinder, that is, the cylinder in which pressure is produced by the motion of the piston, is at room temperature, as in most of my experiments. This cylinder connects through a fine pipe with the lower cylinder, in which is the resistance to be measured, and which is immersed in a vacuum flask with liquid oxygen. The internal diameter of the working high pressure cylinder is 5/16 inch and the length of stroke 3 inches; the diameter of the lower cylinder containing the resistance specimen is 5/16 and its length 5/8 inches. These dimensions are evidently such as to permit building up a high final

pressure if there is no leak.

Much time was spent in finding how to make tight connections and electrically insulated joints at low temperature. By far the simplest electrical set-up would be to take the leads of the resistance out through a plug screwed into the lower cylinder, as in my measurements at higher temperatures. The ordinary construction for the electrically insulated plug proved, however, absolutely unworkable at low temperature, the rubber by which mechanical tightness was secured becoming so hard and brittle as not to function. Efforts to modify the dimensions or to find other materials were unsuccessful, and finally the attempts to take the leads out through the cold cylinder were abandoned, and the leads taken out through the connecting pipe to the upper cylinder, at room temperature, as had once before been done when measuring resistance at a temperature so high as to char the rubber insulation. The problem of getting the insulated leads out of the upper cylinder will be discussed later.

The proper packing of the connecting pipe proved unexpectedly difficult. At higher temperature the problem of packing offers no difficulty at all when the principle of the "unsupported area" is used. Almost anything depending on this principle is successful; if rubber washers are used they may be whittled out in the crudest way with a jack knife, and even careless machine work on the metals parts is not fatal. But the viscosity of a gas is so low that it will escape at high pressure through almost molecular holes, and packings which are sufficiently plastic to close the ordinary imperfections and scratches to leakage by an ordinary liquid are freely permeable to compressed helium. My first connecting pipes were made for the ring type of packing of my ordinary high pressure apparatus, in which, after sufficiently high pressure has been reached to induce plastic flow, the eventual packing is provided by a soft steel ring forced by the pressure against a hardened conical shoulder on the pipe. This had to be given up, for although it could be made to work sometimes, it proved

too uncertain. It was replaced by a lead packing, lead retaining its fluidity under pressure and at low temperature very much better than

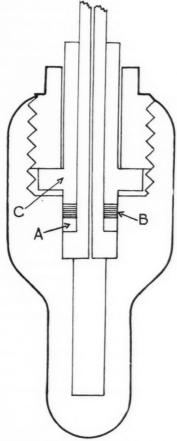


Fig. 1. The lower cylinder and connecting pipe and packing. A is lead cast around the pipe and B split discs of iron or nickel. The hardened retaining piece C is also split.

anything like rubber, for example. The packing is sufficiently indicated in Figure 1. It is of a type which I have used before and it has also been used in plugs for closing holes. The head on the end of the pipe has to be made integral with the pipe, and cannot be threaded on. because a thread always introduces weakness, the pipe being very likely to rupture by the "pinching off" effect at the bottom of the thread. The dimensions of the pipe were approximately as follows: inside diameter, 1/32 inch, outside diameter 7/32 inch, diameter of head 7/16, thickness of head 3/16 inch, length 12 inches. The pipe was drilled from the solid rod and then turned true to the hole. The drilling of so long a hole of such small diameter offers some difficulty. but nothing different in kind from difficulties already mastered in making similar drilled pipes of larger diameter. In drilling, the pipe was mounted in a special rotator, running at about 4000 R. P. M., and the drill was fed in by hand. The necessity for a solid head on each end of the pipe introduces obvious difficulties of assembly, which were overcome by various devices. The lead packing rings were cast in position around the pipe and turned to size. In the normal packing of this type for use at higher temperatures the lead is retained by a solid washer of mild steel, which in turn is retained by a washer of hardened steel, which again is retained by the screw plug. The washers of soft and hard steel evidently had to be modified because of the geometrical impossibility of slipping them over the heads on the two ends of the pipe. The soft steel washer was replaced by a number of washers of sheet iron or nickel 0.015 inch thick. Each of these discs was split along one radius. By means of this split it could be opened up, snapped over the pipe, and then pressed back to circular form. By staggering the splits of successive discs, the equivalent of a single solid washer was built up. The hardened steel washer of the normal packing was replaced by a split steel cylinder with a heavy flange. The hole in the screw plug was made large enough to slip over the head on the end of the pipe, as shown in the diagram. It will be seen that the entire outward thrust on the split cylinder gets itself transmitted to the screw plug through the medium of a shearing stress tending to cut off the flange at its roots.

This type of packing for the connecting pipe has proved entirely satisfactory, when used with proper precautions. Among these it is important that the bearing surface in the cylinder against which the lead is forced must be polished and free from scratches.

The order of the experiment was usually a series of measurements

at CO<sub>2</sub> temperature followed by those at 90° Abs. It proved to be necessary to tighten the screw plug as much as possible after the run at CO2 temperature to overcome the effect of the differential contraction between iron and lead on cooling to 90° Abs. At first it appeared that the only way to reach simultaneously low temperatures and high pressures without leak was to raise the pressure at room temperature to perhaps 5000 kg, a pressure so high that the lead is forced plastically into all the crevices, and then to lower the temperature. But this has disadvantages, it being impossible to make resistance measurements on the first application of pressure at low temperature in this way, and also there is considerable danger in the manipulations incidental to getting the liquid oxygen in place and the temperature adjusted while the pressure is in the apparatus. procedure of tightening the packing between runs has none of these disadvantages, but on the other hand there are sometimes leaks. However, success was attained often enough to outweigh the disadvantages of the other procedure.

The dimensions of the lower cylinder are sufficiently indicated in the diagram. They were so chosen as to reduce the weight of metal

to the minimum consistent with safety.

All the packings at the upper cylinder, which remains at room temperature, were made with rubber, there being no rigidity to hinder at this temperature as at lower temperatures. Care is necessary even under such apparently favorable conditions as these. The rubber washers must be smooth and geometrically perfect; the procedure was finally adopted of cutting them in the lathe with a special knife. The holes in the cylinder which receive the rubber washers must also be smooth and polished. It was found to pay to polish the holes before each assembly with a special polishing tool mounted on a dentist's flexible shaft.

The electrically insulated connections were all made in the top cylinder, one for the manganin gauge coil with which pressure is measured, and three connections to the specimen in the lower cylinder, the fourth current connection to this specimen being grounded to the cylinder. Hitherto the insulated connection has been made through a special plug, carrying on its axis an insulated lead. The plug could be made up separately and then screwed into place in the cylinder. This procedure was now abandoned in order to save room, since the entire apparatus had to be kept small in order to minimize the quantity of gas used. Figure 2 shows the new arrange-

ment. The central stem is solid and insulated from the walls of the cylinder by bakelite, mica, and rubber as shown. As in the previous design of plug, the mica is so disposed as to carry the largest part of the mechanical stress. It is essential that the spaces between the

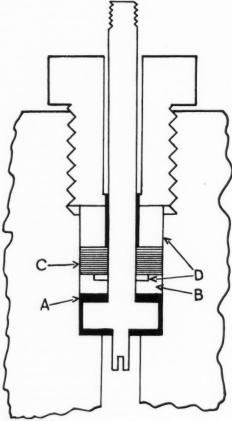


Fig. 2. New type of insulating lead adapted to be directly screwed into the cylinder. A is bakelite, B soft rubber, C mica, and D hardened steel.

stem and the upper hardened steel washer and between the head of the stem and the cylinder be as thin as is consistent with good insulation, or otherwise the soft rubber packing shears off a ring of mica. The diameter of the head must be a larger fraction of the diameter of the solid stem than when pressure is transmitted by a liquid in order that the excess pressure developed in the rubber by the principle of the unsupported area be sufficiently great to overcome the rigidity of the rubber and prevent the gas from leaking. In assembling it is necessary to take the same precautions as with the other type of assembly. The entire cylinder is baked at a temperature of 130° C immediately before assembling to get rid of moisture, the various washers are similarly baked, and the assembly is made with tweezers, taking care not to let the moisture of the fingers get on any of the washers. After assembly the insulation was tested on a bridge sensitive to 100 megohms, and the insulation required to be as good as It was checked by blank experiments that this insulation is

maintained under pressure.

The three lead wires to the specimen in the bottom cylinder are each of enameled copper 0.005 inch in diameter. The three wires are twisted together into a single rope and then bound together with two or three coats of insulating enamel baked on. Considerable difficulty was found before a suitable method of dealing with the leads was developed. It is necessary that the wire be fine and that the insulation be perfect. The finer the wire, the greater the ratio of perimeter to cross section, and the greater the danger of rupture under the viscous drag of the gas as it passes through the pipe from the upper to the lower cylinder. Silk covered wire was found to be too clumsy; the viscous drag of the gas is so great that rupture frequently occurred, and also there were frequent short circuits due to the breaking through of the insulation where one wire rubbed on another. The use of insulating enamel instead of silk, and also the device of binding together the three wires with enamel, thus increasing the ratio of cross section to perimeter, solved the problem sufficiently well. However, a triple stranded lead made of this wire should not be used for more than two runs, the enamel cracking off at the bends. It is always necessary to carefully test the insulation of each strand before assembling.

The method of assembling was as follows. At the lower end of the central hole in the upper cylinder and just above the end of the connecting pipe there is an insulating block of bakelite bearing three

brass ferrules, each of which is soldered to one of the strands of the triple conductor. Just below the ferrules there are three small pockets in each of which a short length of one of the strands of the conductor is coiled. The function of this is to allow some longitudinal motion of the conductor in the pipe as gas passes back and forth. If there is sufficient force to produce longitudinal motion, the conductor uncoils a little out of its pocket, instead of breaking off at the soldered connection. Each of the ferrules registers exactly with the center of one of the side holes through the cylinder and its insulated plug. This plug bears on its end a prolongation in the shape of a piece of brass wire, which is split and the prongs spread. When the plug is pushed home the prongs are forced into the brass ferrules, thus making a spring connection which has sufficient flexibility to allow for the outward motion of the plugs when pressure is applied, compressing the various washers. The resistance specimen is now ready to attach at the lower end. The specimen was usually in the form of wire about 30 cm. long, wound on an insulating spool, usually of "pipe stone." This spool is held in position against the lower end of the pipe with a hollow screw, threading into the end of the pipe, through which passes the triple conductor. The three strands of the conductor are bent around and soldered to the terminals of the specimen, and the fourth connection is made by soldering across to the pipe. The whole is finally protected by a layer of paper, and then the bottom cylinder slipped into place over the spool, and the screw plug turned home.

The manganin gauge was made of wire 0.003 inch in diameter obtained from the Driver Harris Co. The German manganin which I have used in all my other high pressure gauges was not advantageous because of its larger diameter, 0.005 inch, which would have resulted in smaller electrical sensitivity because of the lower resistance possible in the space available. The new manganin was calibrated over the entire pressure range against the old, and the relation found to be linear within 0.1%, approximately the accuracy of the measurements. This is very much more satisfactory than some manganin of American origin which I tried to use for gauges a number of years ago, and which had, among other defects, large wanderings of the zero. Evidently the quality of American manganin has by now sufficiently improved so that it may be used for pressure gauges with as satisfactory results as the German manganin. The composition of the American manganin cannot be quite the same as that of my German manganin, however, for its pressure coefficient of resistance is appreciably higher.  $\frac{1}{R_0}\frac{dR}{dp}$  is  $2.290\times 10^{-6}$  (pressure in kg/cm²) for the German manganin, against  $2.379\times 10^{-6}$  for the American.

Another feature not necessary when pressure is transmitted with a liquid is some method of checking each joint for leak during the progress of the experiment. It was found to pay to build around each joint a special leak tester. This was merely a small air tight chamber made of brass tubing, and pressed by a spring against a rubber washer which separated it from the cylinder, connecting through a small side tube to a nozzle opening under water. Leak was disclosed by bubbles rising through the water. The electrical connections were brought out through split rubber plugs in the ends of the leak testers. Five leak testers were used, four for the electrically insulated leads and one for the connection of the pipe into the top cylinder. The pipe connection to the lower cylinder was immersed in liquid oxygen and thus automatically provided its own test for leak. In addition to the stationary connections, the moving plug on the end of the piston might leak; leak here could be detected with a little Nujol painted on with a brush where the piston enters the cylinder.

Behavior of Steel under High Helium Pressures. With the technique outlined above measurements were made to a maximum pressure of a little over 7000 kg/cm<sup>2</sup>. The pressure limit was set by the rupture of the steel. It was very soon found that helium under high pressures ruptures the containing vessels, as had been feared. A great deal of preliminary work was done in trying to find the cause of this rupture, and to devise means to prevent it. Special tests were made on about a dozen different grades of steel. Rupture usually took place in the neighborhood of 6000 kg/cm.<sup>2</sup> This rupture might take various forms. Sometimes a fine seam was opened along a radial plane, so fine as to be hardly visible; at other times the cylinder was shattered into small pieces. The appearance of the ruptured surfaces was always different from the appearance when the rupture is produced with hydrogen, and the conclusion was soon drawn that the action was not chemical, as in the case of hydrogen, but mechanical. At first I thought that it might be connected with the hardening of the steel, since it is known that the density of hardened steel is less than that of untreated steel. Measurements of the densities of several of the specimens of steel showed a negative correlation between the change of density on hardening and ability to withstand helium pressure without rupture. Finally a steel was found, a Cr-Mo steel,

which successfully withstood the action of 12000 kg without rupture. It is true that this pressure was not supported indefinitely, as would have been possible with a liquid, but instead, the pressure at constant volume dropped back slowly from 12000 to 10600. However, there was no evidence of leak, and this performance was so much superior to that of any other grade of steel tried that further search was discontinued, and a complete apparatus made of this grade of steel, comprising lower and upper cylinders and connecting pipe. test cylinder, which had successfully withstood 12000, was 2 inches in diameter, whereas the upper cylinder of the final apparatus was 4.5 inches. The larger size was needed to provide for the screw connections of the insulating plugs, a feature not necessary in the test cylinder, which could therefore be made smaller. My disappointment was great when the upper cylinder ruptured on the first application of 6000. Various other cylinders were now made from the same grade of steel; one was cut from another bar of the same size, one was from a bar originally of smaller diameter forged up to the required size, and one was from a special forging made by the manufacturers with every precaution to obtain as homogeneous a piece as possible. All of these cylinders broke at about 6000 on the first or second application.

About this time I learned about the "hot acid" method of testing steels, now being used by a number of manufacturers to detect comparatively large scale imperfections, such as inclusions of slag, or particularly regions in which manganese sulfide is segregated. The hot acid test consists in immersing the steel for about 45 minutes in 50% HCl solution at a temperature of 160° F. Imperfections are shown by the more rapid attack of the acid, perfectly sound metal being almost untouched. Application of this test showed at once that the bars from which the 4.5 inch cylinders had been made had marked imperfections toward the center, and that the 2 inch bar, from which the successful test cylinder had been made, was very markedly more homogeneous. In general it appears that the smaller bars, which have been more reduced in diameter from the original billet, are more likely to be homogeneous, but this is not universally the case.

The hot acid test now provides the surest guide that I have found as to whether a given piece of steel is likely to be successful, and I now subject all bars to this test before machining them. Some manufacturers make a special point of providing steel homogeneous to this test, and much may be done by using only such steels, but this is not sufficient, and independent test is always desirable. Also, much may

be done by using the proper grades of steel. The Cr-Va steel, of which I have constructed all my high pressure apparatus for use with a liquid as transmitting medium, is particularly likely to be "dirty," and I have had no luck in constructing gas apparatus from it, and have now discarded it entirely. Cr-Mo steel is much more likely to be clean. The cleanest appearing steel which I have found is a Cr-Ni steel, but this has not yet been adequately tested for high pressure gas use, as it is a recent discovery.

In obtaining the final measurements recorded below, at least six lower cylinders were used, and three or four connecting pipes. During all these breaks of the lower part of the apparatus I was exceedingly fortunate in using only a single upper cylinder. The design of this was modified from that described above, so that instead of a large cylinder 4.5 inches in diameter, a smaller one of 2 inch diameter could be used. This has at once the considerable advantage of starting from presumably sounder metal. In the new design the screw plugs for the insulating plugs were not carried in the walls of the cylinder itself, but in a heavy ring girdling the cylinder and a push fit for it. It is this feature of design which made the smaller diameter possible. material of the 2 inch upper cylinder was "S-M" steel (silicon-manganese) from the Carpenter Steel Co. It is a water hardening steel; it was quenched from 1650° F and then drawn at 750° F to a Rockwell hardness of 51. It was then subjected to a preliminary pressure treatment, first to a pressure of 13500 kg at room temperature with petroleum ether as the transmitting liquid. There was slow yield at this pressure, as there always is, but pressure was maintained by pumping as necessary for nearly 24 hours, and after this time the yield had nearly ceased. It was then further seasoned by subjecting to pressure exerted by nitrogen at room temperature. My idea was that a preliminary treatment by nitrogen might plug the pores in the steel to penetration by helium, because of the much greater size of the nitrogen molecule as compared with the helium atom. The action during the treatment with nitrogen was entirely consistent with the hypothesis that gas was being forced into the pores. Marked dropping of pressure, but with no detectible leak, began in the neighborhood of 8000 kg, much lower than the pressure to which the steel had been accommodated by the previous treatment with petroleum ether. By slowly pushing in the piston, it was possible to build up the pressure, after every increase the pressure dropping back to a value higher than the previous maximum, until in the

neighborhood of 10500 kg, after about 24 hours exposure, the dropping back after every increase became so much accelerated that I did not dare go any higher, and judged that the steel had about reached its limit for nitrogen. This decision was strengthened by a curious whistling noise at 10100, perhaps due to escape of gas through the cylinder. The permanent loss of volume during the seasoning, as shown by the permanent displacement of the piston, indicated that the gas had been forced into the pores of the steel. This agrees with previous results which I had found during measurements of the volume of gases at room temperature, and is a source of error in high pressure gas work which should be carefully guarded against.

The upper cylinder, treated as above, was surprisingly successful, and outlived, as already mentioned, six lower cylinders and several connecting pipes, the pressure with helium being regularly pushed to about 7500 kg/cm<sup>2</sup>. In fact, from one point of view, the cylinder was too successful, because I had no opportunity to try several other cylinders of other grades of steel which I had already constructed

against emergency, and which would have been instructive.

It can be understood that with rupture so frequent an occurrence there may be considerable danger in experiments of this kind. This was guarded against by surrounding the apparatus with heavy steel plates, arranging mirrors to see the critical parts of the apparatus, and taking care to stay on the right side of the plates while pressure was high. However, the manipulations of closing the valves of the bye-pass etc., had to be made at pressures of about 2500, and there were occasional ruptures at pressures even as low as this. These low-pressure ruptures, however, nearly always followed a previous application of a higher pressure. Various secondary lines of defense guarded against explosions at these low pressures, and care was always taken to make the necessary manipulations as quickly as possible.

Temperature control of the lower cylinder had to be fairly close, as otherwise the chance fluctuations of resistance with temperature mask the changes produced by pressure. Constant temperature baths at solid CO<sub>2</sub> and liquid oxygen temperatures proved adequate; liquid air itself proved absolutely out of the question. Commercial solid CO<sub>2</sub>, "dry ice," was pounded to nuggets about the size of a pea, and packed around the lower cylinder in a thermally insulated vessel about 15 cm in diameter and 20 cm deep, and wet with the minimum amount of acetone, to facilitate heat transfer. The liquid oxygen was made by passing compressed oxygen from a commercial tank, about

99.5% pure, through a copper spiral immersed in liquid air. In the interest of economy the spiral was built on the principle of an interchanger, the escaping evaporated air precooling the oxygen as it enters from the tank. At first a great deal of trouble was encountered from stoppage of the oxygen pipe, but by taking out the liquid oxygen at the bottom and arranging the spiral so that flow always had a downward component, the condensed particles of ice or other solid matter were swept along with the oxygen current, and stoppage avoided. The liquid oxygen was placed in a vacuum flask of about 6 cm diameter and 25 cm length. The duration of the experiment was so short, usually about 90 minutes, that the initial supply of oxygen in the flask could be used without renewal, a feature desirable from the point of view of safety, if nothing else. The major source of heat leak was, of course, conduction along the pipe. The level of liquid oxygen was kept constant during the experiment by means of a diving belt arrangement attached to the lower end of the lower pressure cylinder. As oxygen evaporated, air was forced into this diving bell, raising the level of the oxygen in the flask. This manipulation was done by an assistant, who continually (during the experiment) watched the level through a peep hole.

It is an advantage of the potentiometer method of measuring resistance that the measurements are not sensitive to the resistance of the leads, that is, to the level of the oxygen around the pipe. In the preliminary work an attempt was made to measure the resistance by a bridge method with only two leads, and then great difficulty was encountered because of fluctuation of resistance due to the fluctuation of the level of the oxygen on the pipe. The adequacy of the final method of temperature control is shown by the self consistency of the readings and the good recovery of the zero, which never showed any displacement that could be ascribed to temperature drift.

The barometer was read during every run, and slight corrections, given in International Critical Tables (I. C. T.), were applied for the change with pressure of the boiling point of oxygen and the sublimation point of CO<sub>2</sub>. The boiling point of O<sub>2</sub> at 760 mm was taken to be  $-182.95^{\circ}$  C, with a change of  $0.32^{\circ}$  for a one inch change of the barometer. The sublimation point of CO<sub>2</sub> was taken to be  $-78.50^{\circ}$  C, with a change of  $0.405^{\circ}$  for one inch change of the barometer. No allowance was made for the effect of acetone on the sublimation point of CO<sub>2</sub>, as there do not seem to be adequate data on this subject. Landolt and Börnstein, Vol. I, p. 631, give figures from the old work

of Cailletet and Collardeau for the temperature of solid  $CO_2$  when mixed with various liquids, which are obviously wrong, and too high by from  $5^{\circ}$  to  $10^{\circ}$ , as could be shown by direct measurement with a toluol thermometer. In the absence of suitable data, and in view of the fact that the amount of acetone was comparatively small, it seemed safest to use the figures for pure  $CO_2$ .

In the preliminary work the question was investigated whether it would not be possible to replace the pure helium gas with a mixture of helium and nitrogen, the idea being that the freezing point of the nitrogen might be sufficiently depressed by the helium, and at the same time the nitrogen might plug the pores of the steel and so prevent rupture. The method used in this investigation was much the same as that used at Leiden<sup>4</sup> and also by Simon<sup>1</sup> and his collaborators in determining the freezing curve of pure helium. Both upper and lower cylinders were maintained at room temperature, and each was provided with a manganin pressure gauge. A receptacle for liquid air was built around the middle of the connecting pipe. Both gauges were read as pressure was increased by forcing the piston into the upper cylinder. Freezing of the transmitting medium of mixed helium and nitrogen produces a stoppage in the connecting pipe, with the result that the lower gauge remains stationary while the upper gauge rises. It was found in this way that a mixture of 44% N2 and 56% He by volume is frozen solid at about 3000 kg/cm<sup>2</sup> in liquid air. No attempt was made to find whether stoppage occurred also at lower pressures, it being obvious that the mixture was not a practical transmitting medium for my experiments. The freezing pressure of pure nitrogen at 90° Abs. has been found by Simon to be about 1500 kg/cm<sup>2</sup>. An interesting subject for further investigation would be to find whether the freezing of nitrogen-helium mixtures is governed by some sort of partial pressures law, a possibility which is not ruled out by these observations. It seems more probable to me, however, that the nitrogen separates out nearly pure, with little depression of its normal freezing point, because of the chemical inertness of helium.

Several times, particularly during the preliminary work, the connecting pipe clogged at 90° Abs at less than the maximum pressure of 7000. The reason for this was not always plain. One would suspect moisture or other impurities which might be in the helium, which was commercial helium of 99% purity obtained from the Matheson Co. An attempt was made to condense moisture out of the helium by passing it through a very fine capillary at liquid air temperature, but

there was not enough condensation to produce stoppage, and this source of the difficulty is probably negligible. On a couple of occasions the difficulty was definitely traced to imperfect rubber washers in the separator by which the first stage of compression was produced, which allowed the merest trace of the mixture of glycerine and water used as a pump liquid to creep along the cylinder walls into the gas chamber, where it vaporized with enough vapor pressure to plug the connecting pipe on condensation. More careful oversight of the condition of the washers and more frequent renewal removed this difficulty. Toward the end of the experiments recorded in this paper the difficulty rather increased. The last measurements were made in June when the natural humidity of the air was high. Since the separator and intensifier usually contained at the start atmospheric air, this may have had something to do with the trouble, but flushing the system by a preliminary admission of helium did not eliminate the difficulty, and the explanation is not yet plain. It may be connected with the fact that toward the end of the experiments the helium pressure in the tanks

was getting low.

Experimental Procedure. The order of experiment was usually as follows. First the lower cylinder was packed in ice and the resistance measured at atmospheric pressure at 0° C. Temperature was then lowered by packing the lower cylinder in solid CO2 and acetone, and pressure applied, using nitrogen to transmit pressure at this temperature. Readings of resistance at this temperature were made at atmospheric pressure, the tank pressure of the nitrogen, at the end of the separator stroke, about 700 kg, at 1500 kg, at the end of the intensifier stroke after the bye-pass valves were closed, usually between 2000 and 3000, and then at intervals of 1000 kg up to 7000 and back again to 2000, the lowest pressure possible without uncovering the bye-pass and losing gas. The points were plotted as they were measured, and it was almost always found that there was much hysteresis between increasing and decreasing points. This is evidently the seasoning effect of the initial application of pressure which I have always found before in all measurements of the effect of pressure on resistance. A second application of pressure was then nearly always made from 2000 up to the maximum of 7000 and then back again. It almost always turned out that hysteresis disappeared on the second application of pressure, the up and the down points agreeing. If this was the case, pressure was then released beyond the bye-pass, back to zero, and the readings between 2000 and 0 obtained during the last decrease

were accepted as correct. A few times a third application of pressure had to be made before the readings became reproducible. reading was then checked in ice at atmospheric pressure, temperature was then lowered with liquid oxygen, and the sequence of readings above repeated, except that pressure was now transmitted with helium instead of with nitrogen. Another important difference was that the first seasoning application of pressure was hardly ever necessary, but on the first application of pressure at 90° Abs. accommodation was complete, the up and down points lying together, except for an important effect at the zero, to be discussed later. This difference was not entirely due to the previous pressure seasoning at CO<sub>2</sub> temperature, but was at least in part a specific effect of the lower temperature, for on several occasions the order was reversed, and the first run was made with liquid  $O_2$  and the second with  $CO_2$ . On these occasions the first run with liquid oxygen was without hysteresis, while seasoning was necessary at CO<sub>2</sub> temperature in spite of the previous application of pressure at liquid oxygen temperature.

It is a great advantage of the small size of the apparatus and the increased thermal conductivity of metals at low temperatures and of gases at high pressures that temperature equilibrium was reached almost at once after every change of pressure, so that good readings could be obtained as fast as the adjustments of bridge and potentiometer could be made. This was especially the case at liquid oxygen temperature; at CO<sub>2</sub> temperature it was necessary to verify that a steady state had been reached before the reading could be accepted. At liquid oxygen readings could be made about every 4 minutes,

while with CO<sub>2</sub> a minute or two more might be necessary.

In one other respect thermal effects are strikingly different at the temperature of liquid oxygen from what they are at room temperature. On several occasions there was a minute leak at the lower connection, so small that the bubbles could just be seen rising through the liquid oxygen, and much too slow to be detected by any drop of pressure on the gauge. On such occasions the resistance reading was off by a large amount, indicating an enormously increased Joule-Thomson effect under these conditions. This situation would be worth investigating further for its own sake.

There follows now the detailed presentation of data.

# DETAILED PRESENTATION OF DATA.

With one exception the metals measured in this paper belong to the cubic system. They have, therefore, the same compressibility and pressure coefficient in every direction, so that measurements on polycrystal wire give without error a complete description of the behavior under pressure. The one exception is magnesium, which crystallizes in the hexagonal system; previous measurements on this have shown that it is very nearly isotropic with respect to compressibility and resistance, so that little could be gained by using single crystals of this metal. I intend to devote another paper to the markedly non-cubic metals; these must be measured as single crystals, and measurements made in different orientations. Such measurements have already been made on Zn and Bi.

In the following, the arrangement of the metals is the same as in my first paper on the pressure effect of resistance, namely in the order

of melting points.

Lead. For this metal I am indebted to Professor G. P. Baxter, who prepared it in connection with atomic weight determinations. It was extruded into wire 0.009 inch in diameter, of the regular length of about 30 cm, and wound as usual on an insulating spool. The leads were soft soldered. Three sets of runs were made; the first two were incomplete, being terminated by the explosion of the upper cylinder; they do not differ within the limits of error from the results of the third and final run, to which alone the following description

applies. The seasoning effect of the first application of pressure at  $-78.5^{\circ}$ amounted to an increase of relative resistance of 0.8% of the total resistance, or 8.8% of the total change of resistance produced by This comparatively large change of zero at liquid oxygen temperature was accompanied by a very much smaller permanent change of resistance at atmospheric pressure at 0° C, which was increased by less than 0.1% after the run at  $-78^{\circ}$ . At  $-183^{\circ}$  the permanent change of zero produced by the first application of pressure was inappreciable, so that a single run was adequate at this temperature. After seasoning had been completed, the points at both temperatures lay very smoothly, the maximum departure from a smooth curve at  $-78^{\circ}$  being 0.4% of the total pressure effect, and twice this amount at  $-183^{\circ}$ . The relation between pressure and change of resistance was distinctly not linear at both temperatures, there being a departure in the normal direction, that is, the pressure coefficient becomes less numerically with increasing pressure. The effect was small, however, and the second degree term in the following formulas must be recognized to be uncertain by perhaps 30%. The datum

given by the measurements with the greatest accuracy is the mean pressure coefficient between 0 and 7000. The results are:

At 
$$-78.5^{\circ}$$
,  $-\Delta R/R(0, -78.5) = 13.58 \times 10^{-6}p - 9.9 \times 10^{-11}p^2$ .  
Average coefficient  $0\text{--}7000 = -12.88 \times 10^{-6}$ .

$$\label{eq:At-183} \begin{split} \text{At} - 183^{\circ}, \, -\Delta R/R(0,\, -\, 183) \, = \, 13.81 \, \times \, 10^{-6} p \, -\, 15.0 \, \times \, 10^{-11} p^2. \\ \text{Average coefficient 0-7000} \, = \, -\, 12.76 \, \times \, 10^{-6}. \end{split}$$

At atmospheric pressure the relative resistances at  $0^{\circ}$ ,  $-78.5^{\circ}$ , and  $-182.95^{\circ}$  were 1.0000, 0.6880, and 0.2985. I. C. T. gives 1.0000, 0.6899, and 0.2953 as the mean of several observers.

Magnesium. I am indebted for this material to the courtesy of Dr. Zay Jeffries and Mr. L. W. Kempf of the Aluminum Co. of America. It had been specially purified by vacuum distillation in their Research Laboratories. The analysis showed Si 0.004%, Fe 0.007%. The Al content was not specially determined, but in other similarly prepared specimens it has been found to be seldom present in excess of 0.008%. I formed it into wire 0.009 inch in diameter by hot extrusion through a steel die. Considerable difficulty was experienced in making connections. Spot welding was not successful. The method finally adopted was to wrap about the wire a single turn of fine platinum, and then to pinch this together, practically cutting through the magnesium wire. The resistance of the contact was normally high, but by passing through it a high voltage current from a small magneto before each reading, the resistance was reduced to a sufficiently low and constant value. The irregularity of the readings was somewhat greater than usual, however, and doubtless the reason is to be found at the contact.

The runs were made in the conventional order, with no special incident. After the initial application of 7000 at  $-78.5^{\circ}$ , there was a permanent increase of resistance by 0.73% of its total value, or 21.3% of the pressure effect produced by 7000. The total resistance at the ice point was changed by only 0.18% after the runs at  $-78.5^{\circ}$ . The seasoning at this temperature was found to be practically all produced by the first 3000 kg. The second application at 7000 was without appreciable hysteresis. Within the limits of error the change of resistance is linear with the pressure, the maximum departure from a straight line being 2.3% of the total pressure effect. At  $-182.86^{\circ}$  (liquid oxygen) the first application of pressure was without seasoning effect, except that the zero points all lay high, the maximum deviation

being by 7.3% of the maximum pressure effect. The maximum departure from a linear relation of any other single reading was 4.4% of the total pressure effect. The results are:

At  $- 78.4^{\circ}$ , Average coefficient  $0\text{--}7000 = -4.49 \times 10^{-6}$ , At  $- 182.86^{\circ}$ , Average coefficient  $0\text{--}7000 = -5.89 \times 10^{-6}$ .

The relative resistances at atmospheric pressures in terms of the resistance at 0° C were: at  $-78.4^{\circ}, 0.4649, {\rm and}~at-182.86^{\circ}, 0.1443.$  I. C. T. gives for practically the same temperatures 0.682 and 0.230, taken from a paper by Dewar and Fleming in 1893. Their magnesium

was evidently much less pure than this sample.

Aluminum. For this metal, as well as the magnesium, I am indebted to Dr. Zay Jeffries of the Aluminum Co. of America. It was especially pure stock from the Research Laboratories, and had the following analysis: Si 0.008%, Fe 0.014%, Cu 0.011%, balance Al. It was extruded hot to wire of 0.0093 inch diameter through a steel die, and wound on an insulating spool of the usual length, 30 cm. The

terminals were of fine silver wire, spot welded.

At CO<sub>2</sub> temperature the regular procedure was followed. The permanent change of zero after the first application of 7000 was 0.71% of the total resistance, or 23.5% of the maximum pressure effect. This change of zero at  $-78.5^{\circ}$  was followed by a relative change of resistance at 0° C of only 0.12%. Hysteresis practically disappeared after the first application of pressure at  $-78.5^{\circ}$ . The relation between pressure and change of resistance was sensibly linear, and the maximum departure from a straight line by any single reading was 2.4% of the maximum pressure effect. The first attempt at a run at liquid oxygen temperature was terminated by a rapid leak due to a crack in the lower cylinder. The lower cylinder was replaced by a new one, and a satisfactory run obtained without appreciable hysteresis. There was, however, a stoppage of the connecting pipe at the highest pressure. As usual, the zero lay high, by 5.7% of the maximum pressure effect. The other points were linear, with a maximum departure by any single point of 1.8% of the maximum pressure effect. The results were:

At - 78.4°, Average coefficient, 0–7000, = - 4.71  $\times$  10<sup>-6</sup>.

At - 182.9°, Average coefficient, 0–7000, = - 9.16  $\times$  10<sup>-6</sup>.

At atmospheric pressure the relative resistances in terms of the resistance at 0° C were: at  $-78.4^{\circ}$ , 0.6340, and at  $-182.9^{\circ}$ , 0.1521.

I. C. T. quoting Holborn, gives 0.6480 and 0.189 respectively. My

sample is probably somewhat purer.

Silver. This was some of the identical metal with which my original pressure measurements were made in 1916.<sup>5</sup> It was obtained from the old U. S. Mint at Philadelphia, was "proof" stock, and had been drawn through diamond dies to avoid contamination with iron, and

was doubtless of unusual purity.

 $At - 78.4^{\circ}$  two complete runs were made, hysteresis disappearing on the second run. The maximum width of the hysteresis loop, which was also the displacement of the zero, on the first run was .24% of the total resistance, or 11.4% of the maximum pressure effect. On the second run the relation between pressure and change of resistance was linear, the maximum deviation from a straight line by any single point being 1.6% of the maximum pressure effect. The readings at liquid oxygen temperature gave difficulty. Twice there was leak at the lower connection at comparatively low pressure, so that the oxygen bath had to be removed, the cylinder warmed to room temperature and the joint tightened. After this the leak apparently stopped, and reading's were made to 7000 and back. But these readings were unique in that there was very large curvature in the abnormal direction, and also marked hysteresis, but only a small displacement of the zero. In view of this unusual behavior, the run at liquid oxygen temperature was repeated with the identical sample after two months, but with a different lower cylinder. The results were now entirely canonical; the relation was linear with a maximum deviation from a straight line by any single point of 1.3% of the maximum pressure effect, and the zero lay exactly on the curve, rather unusual. There was stoppage of the pipe at the maximum pressure, 7400, but a good reading was obtained at 7000. It seems highly probable that the anomalous results obtained with the first set-up were due to a minute leak, too small to detect by direct measurement, combined with a very high Joule Thomson effect in He, as has been verified by direct observations on other occasions. The results of the first run at -183were therefore discarded. The final results were:

At  $-78.4^{\circ}$ , Average coefficient 0-7000,  $=-3.46 \times 10^{-6}$ .

At  $-182.9^{\circ}$ , Average coefficient 0-7000,  $= -4.09 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.6820, and at  $-182.9^{\circ}$ , 0.2466 (the two values on the two different runs differed by 0.13% from the

mean). I. C. T. gives at the same temperatures from data by Clay, 0.685 and 0.250 respectively, rather close agreement.

Gold. This, like the silver, was the identical piece of wire which was used in the 1916 resistance measurements. The source of the material was the same, and it doubtless is of the same high purity.

 $At - 78.4^{\circ}$  two applications of pressure were necessary, as usual, to give regular results. The effect of the seasoning was unusual in that the resistance was decreased rather than increased. The magnitude of the change of zero was 0.15% on the total resistance, or 9.3%of the maximum pressure effect. On the second application of pressure the relation between pressure and change of resistance became linear, with a maximum deviation from a straight line by a single reading of 2.4% of the maximum pressure effect. At liquid oxygen temperature it was not possible to get beyond 6000 because of leak at the lower connection, and the maximum pressure at which good readings could be obtained was 4300. In this range the relation was linear and there was no hysteresis; it did not seem worth while to set up again to increase the range to 7000. The maximum deviation from a straight line at this temperature was 2.5% of the maximum pressure effect, and the average deviation of the seven readings, 1.1%. As usual, the zero lay a little high, by 1.8% of the pressure effect. The results were as follows:

At  $-78.4^{\circ}$ , Average coefficient 0–7000,  $=-2.97 \times 10^{-6}$ . At  $-182.9^{\circ}$ , Average coefficient 0–4300,  $=-3.27 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.6917, and at  $-182.9^{\circ}$ , 0.2784. I. C. T. gives 0.6904 and 0.2708 respectively from the best work at Leiden; their gold is evidently a little purer than mine.

Copper. This material is electrolytic copper from the Bureau of Standards, and is the identical material as that used for the measure-

ments in 1916.

At  $-78.4^{\circ}$  only a single excursion to 7000 and back was made instead of the usual two. It was evident that the seasoning process was practically all accomplished by the first 1500 kg, and the points obtained with decreasing pressure all lay on a straight line with a maximum departure of 0.017% of the total resistance, or 1.6% of the maximum pressure effect. The permanent change of zero was a decrease by 0.32% of the total resistance. The ice point was changed by only 0.012% after the run at  $-78.4^{\circ}$ . At  $-182.9^{\circ}$  more points

were taken than usual, because it was necessary to remove the bath and tighten the lower connection after about 3000 had been reached. Except for one discarded point, not explained, and which may have been due to a blunder in reading, there was no hysteresis and the relation between pressure and change of resistance was linear with a maximum departure of 3.7% of the maximum pressure effect. The points with decreasing pressure were markedly more uniform; here the maximum deviation was 1.4%. As usual, the initial zero lay a little high, by about 4.5% of the pressure effect, or 0.073% of the total resistance. The results were:

At  $-78.4^{\circ}$ , Average coefficient 0-7000,  $=-2.14 \times 10^{-6}$ ,

At  $-182.9^{\circ}$ , Average coefficient 0-7000,  $=-3.09\times10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.6692, and at  $-182.9^{\circ}$ , 0.1866. I. C. T. gives, quoting from Henning, 0.6524 and 0.1890 respectively, lower at the first temperature and higher at the second. Such a reversal is not usual, and does not seem to permit any conclusion about the relative purity of the materials.

Nickel. This wire, of 0.0035 inch diameter, had been obtained from the Leeds and Northrup Co. in 1921, and was a product of their Research Laboratory, made especially to have the highest possible temperature coefficient of resistance, and therefore of high purity.

The terminals were fine platinum, spot welded.

At CO<sub>2</sub> temperature the behavior was highly abnormal, and recalled the known great hysteresis and related effects when nickel is stretched by a one-sided tension. The readings obtained during the several applications of pressure are reproduced in Figure 3. Not only is there great difference between the results with increasing and decreasing pressure, but there are also time effects, the resistance creeping for a while after release of pressure. There seems to be a distinct preference for the points to lie on a straight line of definite slope. the decreasing points after the first and second applications and the increasing points of the third application all lying on a line of this slope. Furthermore, there is a distinct tendency for the increasing and the decreasing points to come more closely together as the runs are repeated. The heavy line in the diagram was taken to be that corresponding to complete seasoning, and was assumed to be correct in the final computations. The total change of zero at  $-78.4^{\circ}$  was 0.91% of the initial resistance at this temperature, whereas the change

of zero at 0° C found after the runs at  $-78.4^\circ$  was only 0.068% of the initial resistance at 0°. The seasoning effect, as has been found so many times before but less strikingly, is obviously a local effect, characteristic of the particular temperature, and is not carried as a permanent change to other temperatures. At  $-182.9^\circ$  the abnormalities peculiar to  $-78.4^\circ$  had almost entirely disappeared, the only remnant being a slight permanent increase of resistance at the maximum of the permanent increase of resistance at the maximum of the permanent increase of resistance at the maximum of the permanent increase of resistance at the maximum of the permanent increase of the perman

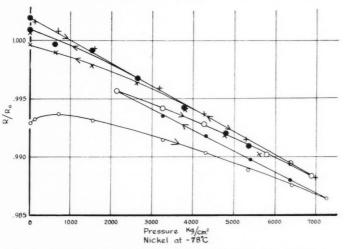


Fig. 3. The relative resistance at solid CO<sub>2</sub> temperature of nickel as a function of pressure. The small open circles show the first application of increasing pressure, the small solid circles the first decreasing pressure, the large open circles the second increasing pressure, the large solid circles the second decreasing pressure, the perpendicular crosses the third increasing pressure and the diagonal crosses the third and last decreasing pressure.

mum pressure, 7400. All the points with increasing pressure lay on one straight line, and those with decreasing pressure on another line of the same slope and higher by 0.06% of the total resistance, or 6.0% of the maximum pressure effect. The maximum departure (except for the zeroes) of a single point from one or the other of these lines was 0.02% of the total resistance, or 2.4% of the maximum pressure effect. The zero, as usual, lay high, but by an unusually

large amount, 0.27% of the total resistance. The results assumed to be best justified by the data are:

At  $-78.4^{\circ}$ , Average coefficient  $0\text{--}7000 = -2.00 \times 10^{-6}$ . At  $-182.9^{\circ}$ , Average coefficient  $0\text{--}7000 = -1.88 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.5938, and at  $-182.9^{\circ}$ , 0.1771. I. C. T. gives, from papers by Fleming in 1900 and Dewar in 1904, 0.613 and 0.208 respectively. My material is evidently considerably purer.

Iron. The same piece of wire was used which had been previously measured for the effect of pressure on resistance in 1916<sup>5</sup> and on thermal e.m.f. in 1918.<sup>6</sup> It was originally drawn down from a bar of American Ingot iron, and was stated to have less than 0.03%

total impurity.

There were various disturbances during the measurements, so that the results for iron are perhaps less satisfactory than for any other metal; however, the results seemed sufficiently secure not to justify repeating the experiment. The new type of upper cylinder was used for the first time for this metal, and on the first run at CO<sub>2</sub> temperature the final form of the CO<sub>2</sub> container and the technique of handling it had not been reached. The most efficient combination of resistances for the potentiometer also had not been worked out. Considerable irregularities on the first attempts at this temperature are doubtless due to inadequacy of temperature control. The last run at - 78.4°, when the final technique for handling the CO<sub>2</sub> had been worked out, showed no hysteresis, as was to be expected because of the previous applications of pressure, but a leak at the lower cylinder set the maximum pressure at this temperature as 4300 instead of the usual 7000. Except for the zero, the points all lay on a straight line with a maximum departure by any single point of 0.13% of the total resistance or 3.0% of the maximum pressure effect. The zeroes were low by 0.07% of the total resistance. It is perhaps worth remarking that after the first and before the final run at  $-78.4^{\circ}$  the apparatus had come to room temperature. that the seasoning effect had been retained is significant. At liquid oxygen temperature a maximum pressure of 6000 was reached. Here a short circuit developed in the manganin gauge, making further readings impossible. The gauge was repaired, and another run made to a maximum of 4400. Here the stem of the manganin plug pinched

off, allowing pressure to leak back nearly to zero. The run was not repeated, but the final results were made up from a combination of the results of the two runs. The relation is linear within the limits of error if one point of the first run is disregarded. Attaching weight to this one point would have demanded slight curvature in the normal direction. Except for the discarded point the maximum departure of a single reading from a straight line is 0.05% of the total resistance, or 4.0% of the maximum pressure effect. The discarded point is too low by 6.0% of the pressure effect. The zeroes did not deviate appreciably from the line. The final results are:

At  $-78.4^{\circ}$ , Average coefficient,  $0-4000 = -2.27 \times 10^{-6}$ . At  $-182.9^{\circ}$ , Average coefficient,  $0-4000 = -2.44 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at 0° C are: at  $-78.4^{\circ}$  0.6029 and at  $-182.9^{\circ}$  - .1639. I. C. T. gives, from Holborn, 0.5770 and 0.120 respectively, considerably lower than my values, and indicative of higher purity. It has been known for some time that the effect of minute impurities on the re-

sistance of iron is unusually high.

Palladium. This was obtained from Baker and Co., their purest. Before use it was heated to 1000° C for 8 hours in a diffusion pump vacuum in order to remove any occluded hydrogen. The pressure coefficient of resistance has been previously measured at ordinary temperatures, but the sample then used was presumably not of high purity, as shown by its low temperature coefficient of resistance. At atmospheric pressure the average temperature coefficient of this new sample between 0° and 95° C was 0.00376, against 0.00318 of the previous sample. This new sample is therefore presumably so much purer that it seemed worth while to redetermine the pressure coefficient at ordinary temperatures, in addition to the regular measurements at lower temperatures. Runs were therefore made in the regular high pressure apparatus to 12000 kg/cm<sup>2</sup> with petroleum ether and kerosene as the transmitting media at 0° and 95° respectively. At 0° the regularity of the readings was sufficient to establish a slight departure from linearity in the normal direction, but at 95° the error was greater and the relation had to be assumed to be linear. At 0° the average deviation from a second degree curve of a single one of the 13 readings was 0.12% of the pressure effect, and at  $95^{\circ}$ the corresponding deviation from a straight line for 14 readings was 0.30%. The numerical results are given below.

At  $-78.4^{\circ}$  the first application of 7000 produced permanent effects, as usual, but hysteresis disappeared on the second application, and the points were linear with a maximum departure by any single point of 0.029% of the total resistance, or 2.3% of the maximum pressure effect. The permanent change of zero produced by the applications of pressure at  $-78.4^{\circ}$  was 0.15% of the total resistance at this temperature, which on warming to  $0^{\circ}$  resulted in an increase of 0.08% of the total resistance at  $0^{\circ}$ . At  $-182.9^{\circ}$  the only incident was the stoppage of the pipe at the maximum pressure; the other points, except the zero, lay on a straight line with a maximum deviation by any single point of 0.06% of the total resistance, or 4.1% of the maximum pressure effect. The zero lay high by about 0.08% of the total effect.

The numerical results are as follows:

At 95° C, Average pressure coefficient, 0-12000,  $-2.052 \times 10^{-6}$ .

At 0°,  $\Delta R/R_0 = -2.166 \times 10^{-6} \mathrm{p} + 5.4 \times 10^{-12} \mathrm{p}^2$ . (Valid to 12000).

Average pressure coefficient,  $0-12000 = -2.101 \times 10^{-6}$ .

At  $-78.4^{\circ}$ , Average pressure coefficient,  $0.7000 = -2.32 \times 10^{-6}$ .

At - 182.9, Average pressure coefficient, 0–6000 = - 2.82  $\times$  10<sup>-6</sup>.

The previous sample of palladium gave at  $0^{\circ}$  an average pressure coefficient between 0 and 12000 of  $-1.95 \times 10^{-6}$ , materially lower numerically than the above, bearing out the universal rule with respect to the effect of impurity on pressure coefficient.

At atmospheric pressure the relative resistance of this new sample of palladium in terms of the resistance at  $0^{\circ}$  C was: at  $-78.4^{\circ}$ , 0.6893, and at  $-182.9^{\circ}$ , 0.2339. I. C. T. gives from Holborn 0.684 and 0.229 respectively, slightly lower than my figures, and indicating

somewhat greater purity.

Columbium. This was obtained from the Fansteel Co. in Chicago. It was 0.0078 inches in diameter, and of the conventional length, 30 cm. The terminals were platinum, spot welded. The pressure coefficient of columbium at ordinary temperatures has been previously measured; the material was obtained from the same source, but since the specimens were not identical, it is probable that the results are not strictly comparable. The purity, as indicated by the temperature coefficient, was doubtless of a lower order than that of any other of the metals measured.

The usual procedure was followed. At  $-78.4^{\circ}$  the first application of pressure produced permanent changes, but the effects disappeared on the second application. The relation between pressure and resistance is linear; the maximum deviation from a straight line of any single reading was 5.% of the maximum pressure effect, or 0.027% of the total resistance. The total resistance was permanently increased by 0.32% of itself by the first application of pressure. At  $-182.9^{\circ}$  there were no appreciable seasoning effects, but the relation was linear on the first application, with a maximum deviation of any single reading of 8.3% of the maximum pressure effect, or 0.036% of the total resistance. The zero did not deviate more than the other points. The results are:

At  $-78.5^{\circ}$ , Average coefficient, 0-7000,  $= -0.98 \times 10^{-6}$ . At  $-182.9^{\circ}$ , Average coefficient, 0-7000,  $= -0.80 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.9344, and at  $-182.9^{\circ}$ , 0.8099. The abnormally low temperature coefficient indicates inferior purity, as already remarked.

Platinum. This was obtained from Baker and Co., their "c.p." brand, for use in resistance thermometry. It was 0.007 inch in diameter, and of the conventional length, 30 cm. It was supplied in the dead soft condition, so that temperature annealing was dispensed with. It was, however, pressure seasoned by an exposure to

12000 at room temperature.

At  $-78.4^{\circ}$  the seasoning effect of pressure was less than usual, doubtless because of the preliminary seasoning at room temperature, and the points with decreasing pressure all lay on a good straight line, with a maximum deviation by any single point of 1.1% of the maximum pressure effect, or 0.012% of the total resistance. It seemed safe to accept this as the correct effect, and a second run at this temperature was not made. The zero was permanently raised by 0.23% of itself by the application of pressure at  $-78.4^{\circ}$ . At  $-182.9^{\circ}$  the usual order of things was reversed, and the points on the first application of pressure were more irregular than usual. This, however, was probably not an abnormal seasoning effect, but was doubtless the effect of a slight leak, which was large enough to be perceptible by dropping of the gauge at the lower pressures, but which automatically stopped when pressure reached the maximum, 7400. The run was repeated, and now the points lay on a

good straight line, with a maximum deviation by any single point of 3.3% of the maximum pressure effect, or 0.042% on the total resistance. The zero was high by 0.06% of the total resistance. The results were:

At  $-78.4^{\circ}$ , average coefficient 0 - 7000,  $= -1.97 \times 10^{-6}$ .

At  $-182.9^{\circ}$ , average coefficient 0 - 7000,  $= -2.34 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.6842, and at  $-182.9^{\circ}$ , 0.2488. I. C. T. gives an elaborate set of tables for the resistance of platinum, from three different samples. The purest of these was "P. T. R. No. 29," measured by Henning, and gave the values 0.6844, and 0.2461 respectively; the first value is practically the same as mine, and the second somewhat lower. The resistances of the two other samples of "pure" platinum quoted in I. C. T. are higher than mine. The purity of this specimen of mine must therefore be judged to be high, although not quite as high as absolutely the best that can be produced.

Rhodium. This was obtained from Baker and Co., was 0.0007 inches in diameter and 30 cm long. Connections were made with platinum terminals by spot welding. Before use it was annealed to a white heat in a gas furnace, and then seasoned by two applica-

tions of 12000 at room temperature.

There were various viscissitudes which make the experimental error larger than usual. On the first application of pressure at  $-78.4^{\circ}$  there was leak at the maximum, which later became worse and made impossible a run with liquid oxygen. The leak was traced to a flaw in the lower cylinder, which was replaced by another. The seasoning effects were unusually large at CO2 temperature, and persisted somewhat more than usual during the second application of pressure. After the termination of the run at liquid oxygen temperature, which went smoothly enough, an attempt was made to repeat the run at  $-78.4^{\circ}$ , but the lower cylinder split on release of pressure at 5000, after readings had been obtained at 7000 and 6000. The initial irregularities were great during this second attempt at CO<sub>2</sub> temperature, showing again that seasoning is a more or less local matter at each temperature. The second run of the first set-up at CO<sub>2</sub> temperature was used in making the final calculations. points are linear, the maximum deviation of any point, except the zero, being 5.9% of the maximum pressure effect, or 0.049% of the total resistance. Both zeroes lay low by 0.085\% of the total resistance. At  $-182.9^{\circ}$  the maximum deviation from a straight line of any single reading except the zero was 4.0% of the maximum pressure effect, or 0.049% of the total resistance. The zero lay high by 0.075% of the total resistance. The results are:

At  $-78.4^{\circ}$ , average coefficient  $0 - 7000 = -1.86 \times 10^{-6}$ .

At  $-182.9^{\circ}$ , average coefficient  $0 - 7000 = -2.26 \times 10^{-6}$ .

The relative resistances at atmospheric pressure in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.6573, and at  $-182.9^{\circ}$ , 0.1935. I. C. T. gives from Holborn 0.658 and 0.201 respectively. My sample is therefore probably a little purer.

Molybdenum. This was the identical piece of wire which was used for my measurements of the effect of pressure on thermal e.m.f. in 1918<sup>6</sup>, and was obtained originally from the General Electric Co., Its mean temperature coefficient of resistance between 0° and 100°

is 0.00461.

The usual order of the experiment was reversed, and the first run was made at liquid oxygen temperature. This run was terminated after a maximum pressure of 6000 had been reached by leak due to the pinching off of the moving plug. The points up to then were fairly good, however. The next run was at CO2 temperature, and here there was no apparent seasoning effect, but on the first application the points lay on a straight line. The maximum deviation of any point, except one discard, was 4.8% on the maximum pressure effect, or 0.025\% on the total resistance. The zero lay on the curve as closely as any other point. The run at liquid oxygen temperature was then repeated, this time successfully, with increasing and decreasing pressure. The points were linear, the maximum deviation of any single reading being 16.4% of the maximum pressure effect, or 0.16% of the total resistance. Both zeroes lay high by an average of 0.12% of the total resistance. The points of the first run at liquid oxygen were much smoother than those of the second, the maximum deviation being only 0.03% of the total resistance. It seemed, therefore, that these should be given more weight in the final result, in spite of the fact that they were obtained only with increasing pressure, and to a maximum of 6000, instead of 7300. The average coefficient from the first run was -1.90 and from the second  $-1.93 \times 10^{-6}$ . The adjusted mean was taken to be 1.91. The results follow:

At  $-78.4^{\circ}$ , average coefficient 0-7000,  $=-1.29\times10^{-6}$ .

At  $-182.9^{\circ}$ , average coefficient 0 - 7000,  $= -1.91 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at  $0^{\circ}$  C were: at  $-78.4^{\circ}$ , 0.6333, and at  $-182.9^{\circ}$ , 0.1582. I. C. T. gives, from a paper by Holborn, 0.665, and 0.230 respectively.

The material of this paper is perceptibly purer.

Tantalum. Two samples of this were used. The first was an old sample originally obtained from the General Electric Co., the pressure coefficient of which had been measured in 1917. At atmospheric pressure its mean temperature coefficient between 0° and 100° was 0.00297, and its average pressure coefficient at 30° between 0 and 12000 kg/cm<sup>2</sup>  $-1.47 \times 10^{-6}$ . This sample was quite hard mechanically, and could not be bent to a sharp angle without breaking. The greatest difficulty was experienced in spot welding to it the platinum terminals, the tantalum becoming so brittle that it almost always broke in handling afterwards. Finally, by using a platinum terminal larger than the tantalum, 0.010 against 0.007 inches, the temperature was kept sufficiently low during the welding so that the brittleness did not become excessive. A single run at liquid oxygen temperature was made with this sample, using one of the primitive lower cylinders, and before the final details of technique had been elaborated. The maximum pressure was only 5000, and the run was terminated by the blowing out of the manganin pressure gauge. The results were quite irregular, the average deviation from a straight line of the six readings being 10% of the maximum pressure effect. The mean coefficient to 4000 was  $-1.08 \times 10^{-6}$ . At atmospheric pressure the relative resistance at this temperature in terms of the resistance at 0° C was 0.406.

The second specimen was obtained from the Fansteel Co. Mechanically, it was entirely different from the first specimen, being soft, easily bent to sharp angles, and furthermore it was easy to spot weld the platinum terminals without producing brittleness. A rough exploration was made of its pressure and temperature coefficients. At atmospheric pressure the mean temperature coefficient between  $0^\circ$  and  $100^\circ$  was 0.00302, only a trifle higher than that of the first specimen, and at  $30^\circ$  the mean pressure coefficient to 12000 was  $-1.42\times10^{-6}$ , slightly lower than the other. The accuracy of this pressure coefficient was not high, however, readings being made only at 0 and 12000.

The regular sequence of readings at low temperatures was made on this sample, and the results were found to be much like those for other metals. At  $-78.4^{\circ}$  the first application of pressure produced

marked permanent effects, but afterwards the points lay on a straight line with a maximum deviation of 2.7% of the maximum pressure effect, or 0.027% of the total resistance. The zero was permanently raised by 0.27%. At  $-182.9^\circ$  the points lay on a straight line on the first application of pressure with a maximum deviation by any single point, except the zero, of 2.3% of the maximum pressure effect, or 0.018% of the total resistance. The zeroes lay high, as usual, by 0.04% of the total resistance. The results are:

At  $-78.4^{\circ}$ , average coefficient  $0 - 7000 = -1.42 \times 10^{-6}$ . At  $-182.9^{\circ}$ , average coefficient  $0 - 7000 = -1.17 \times 10^{-6}$ .

At atmospheric pressure the relative resistances in terms of the resistance at 0° C were: at  $-78.4^{\circ}$ , 0.759 and at  $-182.9^{\circ}$ , 0.416. I. C. T. gives from Holborn 0.729, and 0.332, materially lower, and indicating inferior purity in my sample. It is not probable, however, that the purity of either sample was very high.

It is to be remarked that in spite of the great difference in the mechanical properties there is not much difference in the electrical

properties of the two samples of tantalum used by me.

Tungsten. This was obtained from the General Electric Co., their so-called "C" wire, free from thorium, and was the identical wire which had been used in the investigations of Dr. Blodgett on thermionic emission.

The runs followed the conventional course. No seasoning effect was evident after the first application of pressure at  $-78.4^{\circ}$ . The maximum deviation of any single point, except for the low pressure points below 1000, from a straight line was 1.8% of the maximum pressure effect, or 0.015% of the total resistance. The low pressure points at 0, 100 and 700, however, lay distinctly below the curve, the zero lying off by 0.055% of the total resistance, and on a smooth prolongation of the curve through the 100 and 700 points. If weight is given to the low pressure points, the relation between pressure and resistance departs slightly from linearity, the curvature being in the abnormal direction, and the pressure coefficient increasing numerically with increase of pressure. At  $-182.9^{\circ}$  there was no hysteresis within experimental error, and a single run was sufficient. Here the relation was distinctly not linear, the curvature being evident over the entire pressure range, and being abnormal in direction, as at -78.4°. The experimental points are reproduced in Figure 4. Except for the two divergent points with increasing pressure at 700

and 1500, which may have been a seasoning effect, the maximum departure of any point from a second degree curve is 2.1% of the maximum pressure effect, or 0.018% on the total resistance. The curvature is too great to be ignored at this temperature, and the

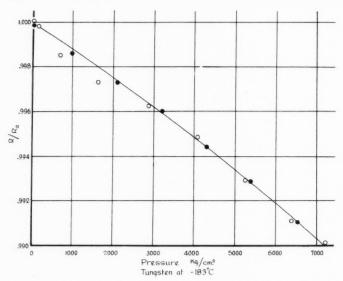


Fig. 4. The relative resistance at liquid oxygen temperature of tungsten as a function of pressure. The feature is that there is marked curvature in the abnormal direction.

measurements are accordingly reproduced by a second degree formula. The results are:

$$\begin{array}{l} \text{At} - 78.4^{\circ}, \, \text{average coefficient,} \, 0 - 7000 = -1.42 \times 10^{-6}. \\ \text{At} - 182.9^{\circ} & \text{average coefficient,} \, 0 - 7000 = -1.36 \times 10^{-6}, \\ \Delta R/R(0, -182.9) = -1.071 \times 10^{-6}p - 4.1 \times 10^{-11}p^2. \end{array}$$

The relative resistance at atmospheric pressure in terms of the resistance at  $0^{\circ}$  C was determined only at  $-182.9^{\circ}$ , the resistance at  $-78.4^{\circ}$  not being calculable because of an oversight in not recording one of the essential resistances. At  $-182.9^{\circ}$ ,  $R/R_0$  was 0.3132.

I. C. T. gives from Holborn 0.195. My specimen, therefore, evidently has considerable impurity.

#### Discussion.

There were two principal possibilities which I had in mind before beginning the experiments. The first has to do with the minimum of resistance at high pressures shown by the alkali metals.<sup>7</sup> The probability was recognized that all metals may have a similar minimum of resistance at very high pressures, and that the pressure of the minimum would be a function of temperature. The question was therefore, whether the pressure of the minimum moves so as to come within reach as temperature is lowered. If such a minimum pressure should prove not to be actually attainable, then evidence as to its probable location would be obtainable from the curvature of the relation between pressure and resistance. Increased curvature in the normal direction as temperature is lowered would mean that the minimum of resistance is displaced to lower pressures at lower temperatures. The second possibility has to do with the temperature of supraconductivity. The temperature at which supraconductivity appears must be a function of the pressure, and the possibility was to be kept in mind that this temperature might be raised as high even as that of liquid oxygen by sufficiently high pressure. There seems at present no general method of telling whether the supraconducting point will be raised or lowered by the application of pressure; it is known that tension raises this point in some metals and lowers it in others, but there have been no measurements on the effect of a hydrostatic pressure.

These two possibilities can be dismissed very briefly. In the first place, no suggestion of supraconductivity was detected. One would expect, perhaps, to find the greatest upward displacement of the supraconducting temperature in those metals which have the highest supraconducting temperature under normal conditions. This was my reason for trying columbium, which is known to have the highest supraconducting temperature of any simple metal, about 8.5° K. The specimen of Cb used in these measurements was not pure, but high purity is of no particular importance, contrary to the first ideas, and Meissner and Franz<sup>8</sup> found supraconductivity in a sample of Cb impure with 1.5% Sn. In the list of 15 metals measured above, three are known to become supraconductors, Pb, Cb, and Ta, and it is probably significant that the pressure coefficient of these three metals becomes less numerically at low temperatures.

With regard to the other possibility, a minimum resistance within reach at liquid air temperature, there is the striking fact that nearly all the metals examined show a linear relation between pressure and resistance. The only instances of definitely established curvature are by lead, in which there is a slight curvature in the normal direction, and tungsten, in which the direction is abnormal, the relative decrease of resistance increasing at high pressure. Appreciable curvature would be expected in the case of lead because of the large numerical value of the coefficient. It does seem, however, that in the case of lead the curvature becomes somewhat less at lower temperatures, the second degree term in the two power expansion for the relative resistance being  $19.0 \times 10^{-11}$  at  $0^{\circ}$  C, 9.8 at  $-78.4^{\circ}$ , and 15.0 at  $-182.9^{\circ}$ . The same is probably true of the other metals, namely, that there is a decrease of relative curvature at low temperatures, although the accuracy is not high, and the effect of the expected curvature is not far from the limits of error. Thus in the case of magnesium, it may be calculated that if the curvature previously found at 0° C also occurs at -78.4°, then a maximum deviation from a straight line is to be expected equal to about the maximum deviation of any of the observed points and about four times the average deviation. It is to be remembered that the accuracy with which deviation from linearity can be determined increases with the square of the pressure range, so that the previous work to a maximum pressure of 12000 gave this term about three times as accurately as the present work to only 7000, to say nothing of other reasons for greater accuracy in the previous work.

The other metals after lead are linear, except tungsten, which shows a distinct curvature in the abnormal direction. One is tempted to see some significance in this in view of the fact that tungsten is the metal with highest melting temperature and highest characteristic

temperature.

Finally, discussion must be made of the previous measurements of Ulrich Fischer.<sup>2</sup> He measured lead, copper, iron, molybdenum, tungsten and the alloy, constantan, at temperatures much lower than mine, in fact, down to liquid hydrogen temperature, but over a much lower pressure range, 150 kg/cm.<sup>2</sup> His pressure was the tank pressure of his hydrogen supply. The pressure coefficients were determined by making a great many measurements of the resistance, first without the tank pressure and then with it. Fischer summarizes his results by saying that the pressure coefficient of resistance increases greatly

with decreasing temperature, and by a greater amount the higher the characteristic temperature of the metal. This summary, however, does not quite reproduce his results; it is true that his coefficient for lead does not begin to increase appreciably until hydrogen temperatures are reached, whereas those of tungsten and molybdenum have begun to increase perceptibly already at CO<sub>2</sub> temperatures, and at liquid air temperatures have doubled, but on the other hand, copper, which has a much lower characteristic temperature than either tungsten or molybdenum, shows a slightly greater increase of pressure coefficient with decreasing temperature. Iron, Fischer does not plot in his final diagram because its purity was not high. Fischer sees in his results confirmation of what he has been led to expect from Grüneisen's empirical expression for the resistance of a metal. Grüneisen<sup>10</sup> found that the temperature dependence of the resistance of a metal at atmospheric pressure can be reproduced by an expression of the type  $R = C \tau F(\tau/\Theta)$ , where F is the Debye function, and  $\Theta$ the characteristic temperature. F approaches a horizontal asymptote for values of  $\tau$  as large or larger than  $\Theta$ , but approaches zero for small 7's. Now Fischer expects the effect of pressure to consist mainly in an increase of  $\Theta$ , the elastic restoring forces and so the general stiffness of the metal becoming greater as the atoms are pushed closer together. Hence the effect of pressure on resistance for a given  $\tau$  will be large if the  $\Theta$  is such that  $F(\tau/\Theta)$  lies in the region in which it is capable of experiencing large changes, and this obviously means the region in which the argument  $\tau/\Theta$  is small or  $\Theta$  large. Tungsten and molybdenum have a large  $\Theta$  and lead a small  $\Theta$ , so that from this point of view Fischer finds his results exactly what he would expect. But these considerations of Fischer seem to take no account of the fact that the C in the formula of Grüneisen may well be a pressure function, and also take no account of the fact that a given increment of pressure may well produce a greater proportional change of  $\Theta$  in a soft metal like lead than in a hard one like tungsten, and thus compensate for the effect of the favorable absolutely high value of  $\Theta$  in tungsten.

But entirely apart from these theoretical considerations, it seems to me that Fischer's experimental values cannot be correct. The effects which he finds are much greater than I find. We agree essentially with regard to lead, which shows very little change of coefficient down to liquid oxygen temperature. But for the other metals Fischer has at liquid oxygen temperature an increase in the pressure

coefficient of tungsten compared with its value at  $0^{\circ}$  C of 77% against my decrease of less than 1%; for molybdenum an increase of 100% against my 47%, for copper 94% increase against my 65%, and for iron 59% increase against my 4%. It is true that the coefficients of most of my metals increase numerically at low temperatures, as shown in Table I, but this increase is not universal by any means,

TABLE I.

AVERAGE PRESSURE COEFFICIENT OF RESISTANCE UP TO 7000 KG/CM<sup>2</sup> AS A FUNCTION OF TEMPERATURE.

	Temperature		
Metal	0°	-78°.4	-182°.9
Pb	$-12.99  imes 10^{-6}$	$-12.88  imes 10^{-6}$	$-12.76 \times 10^{-6}$
Mg	-4.39	-4.49	-5.89
Al	-4.28	-4.71	-9.16
Ag	-3.45	-3.46	-4.09
Au	-2.94	-2.97	-3.27*
Cu	-1.88	-2.14	-3.09
Ni	-1.85	-2.00	-1.88
Fe	-2.34	-2.27	-2.44
Pd	-2.13	-2.32	-2.82
Cb	-1.18	98	80
Pt	-1.93	-1.97	-2.34
Rh	$-1.64\dagger$	-1.86	-2.26
Mo	-1.30	-1.29	-1.91
Ta	-1.45	-1.42	-1.17
W	-1.37	-1.42	-1.36

<sup>\*</sup> Max. press. 4300.

and furthermore, there is no correlation with the characteristic temperature, by far the greatest increase being for aluminum, with a low characteristic temperature, whereas the metals with the two highest characteristic temperatures, tungsten and tantalum, show decreases.

It seems to me that an adequate explanation of Fischer's results can be found in his low pressure range. This I believe to have been too low to sufficiently season the metals. Seasoning effects were always present in my measurements, and in most cases did not disappear until pressures of several thousands of kilograms were reached, twenty times or so higher than the pressures of Fischer. Furthermore, in spite of the fact that complete regularity could be

<sup>†</sup> On a less pure sample.

given to the high pressure readings by proper seasoning, there remained in the majority of cases an irregularity in the zero reading. If the detailed presentation of the results of the seasoning applications of pressure is consulted, which I have purposely made very full in order to permit examination of this point, it will be found that in many cases the zero lies consistently high. It will be recalled that my readings were made at atmospheric, and then at tank pressure, which would be Fischer's maximum pressure. If the zero lies high, a pressure coefficient calculated from the first two readings will obviously be high, and I believe that this is exactly what has happened in the case of Fischer's results. Furthermore, such an effect would be expected to be greatest in a mechanically hard metal, like tungsten. which has also a high characteristic temperature, thus accounting for the apparent correlation with the characteristic temperature, and to be much less in so soft a metal as lead, for which Fischer and I have essentially the same results.

It does not seem to me that the time is yet ripe to speculate on the theoretical significance of these results, since the explanation of the effect of pressure under ordinary conditions, and in particular the minimum resistance, is not at all understood. These results must be taken in the spirit of an addition to our experimental knowledge which will later do their part in assisting to understand the conduc-

tion mechanism.

In general, the results may be summarized by the statement that the pressure coefficient of resistance increases somewhat numerically at low temperatures. It is significant that with the exception of nickel, which is anomalous in other respects, the metals of this paper which have shown a numerical decrease of coefficient at low temperatures are those which are known to be least pure, columbium and tantalum in particular being of inferior purity and investigated only because they exhibit the phenomenon of supraconductivity. With regard to the other metals, there is no correlation which strikes the eye between the magnitude of the change of pressure coefficient with temperature and other properties.

I am indebted to my mechanic Mr. Charles Chase for assistance in setting up the apparatus and making the runs, and to the Milton Fund of Harvard University for financial assistance in procuring some

of the apparatus and other supplies.

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